# Influence of altitude on ozone levels and variability in the lower troposphere: a ground-based study for western Europe over the period 2001-2004

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# Influence of altitude on ozone levels and variability in the lower troposphere: a ground-based study for western Europe over the period 2001–2004

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## Abstract

The PAES (French acronym for synoptic scale atmospheric pollution) network focuses on the chemical composition (ozone, CO, $NO_{x/y}$ and aerosols) of the lower troposphere (0–3000 m). Its high-altitude surface stations located in different mountainous areas in France complete the low-altitude rural MERA stations (the French contribution to the european program EMEP, European Monitoring and Evaluation Program). They are representative of pollution at the scale of the French territory because they are away from any major source of pollution.

This study deals with ozone observations between 2001 and 2004 at 11 stations from PAES and MERA, in addition to 16 elevated stations located in mountainous areas of Switzerland, Germany, Austria, Italy and Spain. The set of stations covers a range of altitudes between 115 and 3550 m. The comparison between recent ozone mixing ratios with those of the last decade found in the literature for two high-elevation sites (Pic du Midi, 2877 m and Jungfraujoch, 3580 m) leads to a trend that has slowed down compared to old trends but remains positive. This could be attribuable to the reduction of ozone precursors at European scale, that however do not compensate an ozone increase at the global scale. Averaged levels of ozone increase with elevation in good agreement with data provided by the airborne observation system MOZAIC (Measurement of OZone and water vapour by Airbus In-service airCraft), showing a highly stratified ozone field in the lower troposphere, with a transition at about 1000 m asl between a sharp gradient (30 ppb/km) below but a gentler gradient (3 ppb/km) above. Ozone variability also reveals a clear transition between boundary-layer and free-tropospheric regimes at the same altitude. Below, diurnal photochemistry accounts for about the third of the variability in summer, but less than 20% above – and at all levels in winter – where ozone variability is mostly due to day-to-day changes (linked to weather conditions or synoptic transport). Monthly-mean ozone mixing-ratios show at all levels a minimum in winter and the classical summer broad maximum in spring and summer – which is actually the superposition of the tropospheric spring maximum (April–May) and




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regional pollution episodes linked to persistent anticyclonic conditions that may occur from June to September. To complement this classical result it is shown that summer maxima are associated with considerably more variability than the spring maximum. This ensemble of findings support the relevance of mountain station networks such as PAES for the long-term observation of free-tropospheric ozone over Europe.

## 1 Introduction

Tropospheric ozone is known as a pollutant since the 1950s, causing harm to human health and ecosystems (e.g. Brunekreef and Holgate, 2002). It also plays a considerable role in the oxidising capacity of the troposphere and acts as the third greenhouse gas in terms of additional radiative forcing at Earth's surface (IPCC, 2001). For these reasons tropospheric ozone levels have been a matter of concern for the scientific community over the last decades. There is considerable interest in quantifying surface background ozone concentrations and associated trends as they may serve to define a lower limit with respect to reductions of ozone by control of anthropogenic precursors. Background ozone has several well documented sources, natural and anthropogenic: i) downward transport from the stratosphere, ii) local photochemical production from its major anthropogenic precursors volatile organic compounds (VOC), carbon monoxide (CO) and nitrogen oxides ($NO_x$), iii) remote production associated with long-range transport. The ozone concentration results from a complex combination of production, transport, chemical destruction and deposition.

Ancient measurements have been used to identify some trends in background levels of tropospheric ozone, as for instance in the study by Marenco et al. (1994). In their study, data from measurements at the Pic du Midi (2877 m) between the 1870s and 1910 and then in the 1980s were used to show that ozone mixing ratios have increased by a factor of 5 since the beginning of the twentieth century, corresponding to an exponential increase at a rate of 1.6%.yr$^{-1}$. Oltmans et al. (2006) showed that ozone at Zugspitze increased of 12.6%/decade (1.3%.yr$^{-1}$) between 1978 and 2004. In

addition, Staehelin et al. (1994) found an increase by a factor of 2 between the 1950s and the 1990s at Arosa (Switzerland). Such increase of ozone levels led European countries to subscribe promises about emissions of atmospheric primary pollutants. Two conventions were signed aiming at reducing VOC (Geneva 1991) and $NO_x$ (Sofia 1988), two major anthropogenic ozone precursors. As a consequence of the application of these conventions, anthropogenic emissions of ozone precursors have actually decreased. In Europe, considerable emission reductions have been made since the late 1980s; they are of the order of 30% for $NO_x$ and NMVOC and of 45% for CO for Europe as a whole (Vestreng et al., 2004; Derwent et al., 2003). Despite these reductions, most authors report an increase of background tropospheric ozone levels in the lower troposphere: for example (Brönnimann et al., 2002) found an increase of the average value of around 0.5–0.9 ppb.yr$^{-1}$ for 13 Swiss stations – some of them above 1000 m (altitude hereafter given above see level) – between 1991 and 1999. Ordóñez (2006) found an increase by around 0.5 ppb.yr$^{-1}$ for 8 alpine stations above 1000 m between 1992 and 2002. Over the past decades there have been contradictory explanations about the origins of surface ozone over Europe and about the spring-time maximum (Monks, 2000). Despite a decline in episodic peak ozone mixing ratio ((e.g. Derwent et al., 2004; Brönnimann et al., 2002) mean ozone mixing ratios continue to rise over Europe. Jonson et al. (2006) give some explanation about the factors affecting European tropospheric ozone trends but conclude that if the increase in winter and the decrease in the magnitude of high ozone episodes may be attributed to the decrease in ozone precursor emissions since 1990, the trend in summer is very difficult to identify from the measurements because of large inter-annual variability. There are still many uncertainties about the evolution of ozone concentrations during the two next decades in the free troposphere; long time series are thus needed. In a first part of the present study we will compare data from the literature of the 1990s to our recent data as a contribution to the discussion on trends over the last decade.

Numerous studies based on surface measurements in Europe have been conducted to investigate background tropospheric ozone, from the points of view of its spatial

variability (e.g. Scheel et al., 1997) and temporal variability at different scales (decadal trends, interannual variability, cycles, etc.) for both low-altitude stations especially on coastal areas, (e.g. Ribas and Peñuelas, 2004; Simmonds et al., 2004; Carslaw, 2005) and high-altitude stations (e.g. Bonasoni et al., 2000; Brönnimann et al., 2000; Schuepbach et al., 2001). In these studies the term "background ozone level" has different definitions but the common idea is an ozone level representative of the atmosphere at large spatial (e.g., hemispheric) or temporal (e.g., monthly) scales, to which natural or anthropogenic perturbations will add at smaller scales. For this purpose the considered stations are chosen away from the influence of direct pollution sources and more or less sophisticated treatments are applied to the data running means, meteorological or trace-gas filters, (e.g. Zellweger et al., 2003).

Mountain stations most often fulfil the condition of being "clean sites" and hence are of particular interest. Regarding the high-altitude sites (typically above 2000 m) it is often claimed that they are "above the boundary layer" or "representative of the free troposphere" by sole consideration of their elevation. However mountains considerably enhance atmospheric turbulence and affect circulation for many reasons (roughness, synoptical lifting, hydraulic effects, thermally-induced circulations, etc.) and thus it can be hardly stated that even a high-moutain station is free from the influence of the surface without further investigation.

It is also known that background ozone level increases with height in the lower troposphere (ozone content being eroded near the surface by deposition and titration that dominates in the boundary layer at the yearly time-scale). Climatologies of vertical ozone profiles have been established from airborne in-situ measurents balloons data, (e.g. Naja et al., 2003);aircraft data, (e.g. Fischer et al., 2006; Zbinden et al., 2006). Few surface-data based studies considering a network of stations in a range of altitude (e.g. Brönnimann et al., 2000) also pay some attention to this stratification. However no extensive comparison still exists in the literature between (airborne) data in the true free troposphere (i.e., unaffected by surface effects) and surface data at equivalent altitude.

The present study aims at investigating the following two questions: (i) To what extent measurements from surface stations ranged in altitude can capture the stratification of background ozone in the lower troposphere? (ii) More generally to what extent an elevated surface station is representative of the free troposphere at similar altitude, in terms of ozone level and variability? For this goal we propose an analysis of ozone data between 2001 and 2004, from not only 27 mountain or rural stations in western Europe ranged in altitude up to 3500 m, but also from profiles above Frankfurt (Germany) provided by MOZAIC (Measurements of OZone and water vapour by Airbus In-service airCraft).

The paper is organised as follows. The networks and datasets are described in Part 2. Part 3 focuses on the trends of tropospheric ozone in Western Europe. Finally, Part 4 analyses the influence of altitude on ozone levels and variability. The conclusions are summarized in final Part 5.

## 2 Description of the observation networks and datasets

Ozone surface data come from:

- 2 French observation networks, MERA and PAES. 8 stations belong to MERA and 3 to PAES.
- 4 Swiss organisations/networks: NABEL (National Air Pollution Monitoring Network) , IAP (Institute for Applied Plant Biology), and the Swiss cantons Bern (BE) and Graubünden (GR). Data of 9 Swiss Alpine stations are provided.
- the World Data Centre for Greenhouse Gases (WDCGG: available on http://gaw.kishou.go.jp/wdcgg.html).

All the sites are displayed in Fig. 1, and details are given in Table 1. Elevations range from 115 m up to 3500 m so that air-masses from the boundary layer to the lower free troposphere are sampled.



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The MERA observation network is the French contribution to the international EMEP Program (European Monitoring and Evaluation Program, http://www.emep.int/). The 8 stations have been settled far from urban, industrial and agricultural pollution sources. The network was designed to monitor ozone concentration and atmospheric wet and dry deposition. These stations are located in both mountainous and flat areas, and are well distributed over the French territory. All of them are in forest and/or grassland rural areas. Their altitudes range from 115 m to 1750 m.

The PAES (french acronym for atmospheric pollution at synoptic scale) network is complementary to MERA with 3 high altitude sites in the Pyrenees, Massif Central and Vosges. It is devoted to photo-oxidant pollution at synoptic scale. PAES stations are away from any major source of pollution, and provide measurements (available on http://paes.aero.obs-mip.fr/paes.html) of ozone and gaseous precursors, CO and $NO_{x/y}$, which are not yet systematically observed in France. Only ozone data from PAES will be considered in this study. The station altitudes range from 750 m to 2877 m. The Pic du Midi (PDM) is an isolated high summit in the Pyrenees; it is located 150 km to the east of the Atlantic Ocean and most of the time directly exposed to oceanic westerlies. It may hence be considered as representative of background conditions of Southern Europe. The Puy de Dôme (PDD) station is also an isolated summit in the Massif Central. The Donon tower (DON) in the Vosges Mountains emerges from a dense forest.

In addition, different Swiss organisations provided ozone data for 9 elevated stations. Time series from 4 sites in the Swiss Air Quality Network NABEL were investigated: Chaumont (CHA), Rigi-Seebodenalp (RIG), Davos (DAV) and Jungfraujoch (JUN). Data of Arosa (ARO), and Castaneda (CAST) were provided by the Swiss canton Graubünden; Zimmerwald (ZIM) by the Swiss canton Bern; finally, Zugerberg (ZUG) and Wengernalp (WEN) by the Institute for Applied Plant Biology. Some of the Swiss sites are described by Staehelin et al. (1994); Brönnimann et al. (2000); Schuepbach et al. (2001).

Finally, we used WDCGG hourly data for 7 additional stations, located in Germany (HOH, SCH and ZSP), Austria (SON), Italia (MDC) and Spain (NOI and SAN).

Ozone data from the different ground stations were taken at various sampling rates (from 5 min to 1 h) using standard UV absorption analysers. A coherent and synchronized dataset has thus been first obtained by averaging data from stations on a hourly basis. Two other datasets derived from the latter are also used in this study: a daily averaged dataset and a monthly averaged dataset.

Data from the MOZAIC program were also used in this study. The MOZAIC program was initiated in 1993 by European scientists, aircraft manufacturers and airlines to collect experimental data. Its goal is to help to understand the atmosphere and how it is changing under the influence of aircraft traffic and more widely of human activity (Marenco et al., 1998). MOZAIC consists of automatic and regular measurements of ozone and water vapour by five long range passenger airliners flying all over the world, with a sampling rate of 4 s, i.e., approximately every 50–100 m along the vertical profiles. MOZAIC data provide, in particular, detailed ozone and water vapour climatologies in the troposphere and lowermost stratosphere since 1994 as well as CO and $NO_y$ since 2001. Details on the measurements performed by the MOZAIC program can be found in Marenco et al. (1998), Thouret et al. (1998) and Nédélec et al. (2003). Ozone measurements during MOZAIC ascent and descent vertical profiles over Frankfurt and Paris for the period January 2001–July 2004 were used in the present study.

## 3 Trends in tropospheric ozone

Marenco et al. (1994) exploited ancient measurements at the Pic du Midi (PDM) station, and showed that the mean ozone concentration in the free troposphere has increased by a factor of 5 since the end of the 19th century, to reach 50 ppb at present. This corresponds to a rate of $+1.6\%.yr^{-1}$. However, ozone levels were in the range of 47–49 ppb between 1990 and 1993 and of 48.3 ppb on average between 2001 and 2004. Thus ozone mixing ratios at PDM seem to stabilize instead of following further the trend



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proposed by Marenco et al. (1994), as shown in Fig. 2.

This result at PDM can be put in wider perspective considering trends at other high-altitude sites in the Alps or also trends observed from MOZAIC measurements over comparable periods. All the results are summarized in Table 2. To estimate these trends we used mean ozone mixing ratios given in the literature and compared them to our recent values. Ozone levels remain stable at MDC (but this result has to be considered cautiously because the covered period is shorter than for the other estimated trends). Ozone levels at JUN (3580 m) increased at the rate 0.4–0.5 ppb.yr$^{-1}$(0.8-0.9 %.yr$^{-1}$); those at SON and ZSP increased at a rate of 0.4 ppb.yr$^{-1}$(0.7 %.yr$^{-1}$) and 0.3 ppb.yr$^{-1}$(0.6 %.yr$^{-1}$) respectively. These estimations are consistent with those by Ordóñez (2006) based on data from 8 sites in Central Alps (Germany, Switzerland and Austria), 3 of them above 2000 m (including JUN, SON and ZSP) and 5 between 1000 and 2000 m (including ARO, DAV, RIG and CHA). For these stations, they found an average increase of 0.5 ppb.yr$^{-1}$between 1992 and 2002 (except in summer).

These trends (increase by 0.5 ppb.yr$^{-1}$since the early 1990s for stations above 2000 m) based on surface data are also consistent with those proposed by Zbinden et al. (2006) based on MOZAIC data. They showed for the trends of integrated tropospheric ozone column over the period 1995–2001 a linear increase by 0.7%.yr$^{-1}$above Frankfurt and 0.9%.yr$^{-1}$above Paris. This motivated the comparisons between surface data and MOZAIC profiles made in this study (see Sect. 4).

In summary, ozone mixing ratios appear to go on increasing in the troposphere over Western Europe, but the ozone evolution in Western Europe does not seem to follow any longer the rapid trend proposed 12 years ago by Marenco et al. (1994). In addition, for some stations such as PDM, no trend is found since the early 1990s, in contrast to the rapid increase between the 1980s and the 1990s. This is probably due to the significant decrease of ozone precursors emissions in Europe since the late 1980s. Finally, it should be noted that the trend established by Marenco et al. (1994) is based on ozone mixing ratios of stations of very different altitude, and therefore should be interpreted with caution. Indeed ozone level and variability strongly depend on altitude



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in the lower troposphere. This is considered in detail in the next section.

## 4 Influence of altitude on ozone levels and variability

### 4.1 Background levels and variability

The mean ozone concentration is known to strongly increase with altitude in the first kilometres of the troposphere (e.g. Brönnimann et al., 2000; Zaveri et al., 1995). Near the ground, ozone depletion is mainly due to surface deposition. It is thus of primary importance to quantify this stratification when considering data from mountainous stations at different altitudes. Therefore, we propose a comparison of the ozone levels as a function of altitude between a set of surface stations with good vertical coverage in the first 4 kilometres of the troposphere and a climatology of MOZAIC vertical profiles. Prior to this, Fig. 3 overlays the mean ozone profiles for 4 years of flights above Frankfurt and Paris (note that MOZAIC flights are less frequent above Paris than above Frankfurt so that Fig. 3 only includes data from commonly covered periods, namely 24 months out of 43 in the period January 2001–July 2004). Both profiles are very similar to each other, which justifies the representativity of Frankfurt for Western Europe and hence that a direct comparison can be done between Frankfurt profiles (with the 43-month complete dataset) and the surface stations over the same 43 months. As Frankfurt MOZAIC take-offs and landings are well distributed within the day (with a frequency of around 70 profiles per month and a minimum of 30 profiles except in March 2001, according to Zbinden et al., 2006), we used the monthly data and hourly associated variability from the surface stations and a monthly mean dataset for MOZAIC for the comparison between them. Figure 4 shows the statistics for ozone levels and variability. Average ozone levels for surface data are in good agreement with MOZAIC. The 3 lowest stations (BRO, TAR and PEY) show a positive bias with respect to the MOZAIC profile. A poorer agreement is expected for the lowest levels, where local effects (e.g., surface deposition) usually play an important role. In addition, the three



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sites are exposed to oceanic air masses while Frankfurt is a continental site. Averaged ozone level strongly depends on altitude and vary from 25 ppb to 53 ppb over the range 100 m–3500 m. The ozone gradient is very steep up to 1000 m (around 30 ppb/km) and gentler but still meaningfull above (around 3 ppb per kilometre).

The change in slope around 1000 m, clearly shown by the MOZAIC mean profile, indicates how deep is the direct influence of surface deposition and boundary-layer chemistry on the ozone level. The striking result here is that also a set of surface stations at different elevations is able to capture this transition in ozone mean stratification despite the fact that each surface station, even at high altitude, is intrinsically under the influence of the surface.

To further investigate this point, we consider ozone variability (standard deviation) as a function of station elevation, on the base of a comparison between hourly and daily data. With the second dataset (daily data) the component of the diurnal photochemical cycle of ozone is indeed filtered out from the calculated variability. So the comparison of both results allows to discriminate boundary-layer photochemistry from the other sources of variability. Results are displayed in Fig. 5. Variability based on hourly data (Fig.5a-b) is maximum at sea level (15 ppb in summer and 10 ppb in winter) and decreases with height in both seasons (8 ppb in summer and 5 ppb in winter at JUN). (Note that this decrease is opposite to the increase of ozone mean level, so it is even more pronounced in relative value – not shown). This result is not surprising because ozone is strongly affected by surface effects and boundary-layer photochemistry. The role of the latter in the variability compared to the contribution of day-to-day changes in ozone level (due to changing weather conditions, transport at synoptic scale, etc.) is made evident considering the ratio daily variability / hourly variability (Fig.5c-d). In winter when photochemistry is not very active the day-to-day changes account for 75–90% of the variability at all levels. Note that this ratio is maximum for some stations at around 1000 m asl. This may be due to the varying depth of the boundary layer according to changing weather conditions. So these mid-altitude stations may be alternatively under the influence of either the boundary-layer or the free troposphere. In summer

the ratio remains in the range 80–90% for stations above 1000 m but drops to only 60–70% below, where therefore diurnal photochemistry takes a considerable part — about the third — of the total variability. Thus the altitude 1000 m asl appears to mark a clear transition from a boundary-layer to a free-tropopheric regime for ozone (at least as observed by surface stations). This is moreover consistent with the change in slope of ozone stratification noted above.

To summarize it can be stated that altitude is a key parameter for surface observation of both mean level and variability of ozone mixing ratio. Ozone mean level is indeed a highly stratified field in the lower troposphere. Hence, estimations of the long term trends should be only done using data from the same site, or at least from sites of comparable altitudes. Photochemistry appears to be the major source of variability in the lowest kilometre, while day-to-day variability peaks around 1000 m. Seasonal aspects of ozone variability are considered in more detail in the following paragraph.

### 4.2 Seasonal aspects

Figure 6 represents comparisons between daily data at surface stations and MOZAIC profiles distinguishing winter and summer. It clearly shows 10 ppb higher ozone values in summer than in winter. During summer, variability is also almost twice as important as during winter likely because of enhanced photochemistry. Indeed day-to-day net photoproduction in the boundary layer during lasting pollution episodes may be exported into the free troposphere. This is precised now with a more detailed seasonal analysis.

The yearly evolution of the monthly-averaged ozone mixing ratios was analysed for the 4 years (Fig. 7). It shows a systematic seasonal variation with minimum values between 10 and 45 ppb in autumn-winter (November–January) from the lowest to the highest station. The first maximum values (between 30 and 70 ppb according to the elevation of the station) are systematically observed during late spring and correspond to the spring tropospheric ozone maximum well documented in the literature (Monks, 2000; Vingarzan, 2004). Depending on the years and also on the stations, between

one and three additional maxima in ozone values may be observed during summer and early autumn according to the variable occurrence of lasting anticyclonic episodes and heatwaves. Such episodes can be evidenced by meteorological observations at PDD (Fig. 8). Each can be linked to ozone peaks at low- or mid-altitude stations and even at high altitude stations in some case in Fig. 7 (episodes marked with arrows). Ozone levels of some mid-altitude stations (between 700 m and 1400 m) thus may sometimes exceed ozone levels at the highest stations (e.g., during the extremely warm and dry summer of 2003). Summer photochemical episodes following the spring (tropospheric) maximum induce a more or less constant ozone level from April to September known in the literature as the broad summer maximum (Ribas and Peñuelas, 2004). Note however that summer pollution episodes occur at local, or at most regional, scale whereas the spring maximum is a hemispheric phenomenon.

The variability associated to seasonal (3-month) statistics on ozone for the 4 years is displayed in Fig. 9. For clarity mean seasonal ozone levels and relative variability based on daily data are represented only for two distinct groups of stations: below 500 m and above 2800 m (the stations inbetween – not shown –have intermediary behaviors). The seasonal cycle of relative variability (ratio of standard deviation to mean level) is quite different for the two groups: at low altitude variability is maximum in winter and minimum in spring; at high altitude, variability is maximum in summer and minimum in winter.

The winter maximum of (relative) variability at low altitude can be explained by low mean levels and in the same time variable deposition and destruction that occur in the boundary layer and cause enhanced variability (e.g. Ordóñez et al., 2005). Contrariwise the high altitude stations are decoupled from the boundary layer and sample mostly free-tropospheric air, which explains low variability (even in relative value).

Relative variability at high altitude reaches its maximum in summer (despite high ozone level). At low altitude it is not as high as winter (it is in fact higher in absolute value – not shown – especially for the "photochemical" summers 2001 and 2003) but however higher than in spring and autumn. Thus variability appears to be enhanced at

all levels. This is due to boundary layer photochemistry, that also (indirectly) affects the highest stations.

Finally the spring variability is at all altitudes lower than the summer variability while ozone levels are comparable (broad summer maximum). (There was a notable exception in 2002 when summer variability was especially low for some stations due to particularly bad weather and weak photochemistry.) Low variability has to be linked to the hemispheric scale of the ozone spring maximum.

To summarize the most commonly observed annual evolution of background ozone level is a first maximum in spring (April-May) linked to the increase of tropospheric ozone at the hemispheric scale, followed by a second one in summer when persistent anticyclonic weather allows enhanced photochemical production in the low levels. The summer maximum is associated with larger variability than the spring maximum, indicating the local or at most regional character of the phenomenon and its link to rapid photochemistry. This result is also valid for the highest stations and hence is an indication that the boundary layer photochemical-production in summer is susceptible to affect the composition of the lower free troposphere for sufficiently lasting episodes.

## 5 Conclusions

The present study – an analysis of 4 years (2001–2004) of ozone data from 27 surface stations in France, Switzerland, Germany, Austria, Italy and Spain – has been the first opportunity to put original databases from two French networks, MERA and PAES, in a European perspective including more widely known sites for ozone measurements (e.g., Jungfraujoch, Zugspitze) as well as airborne MOZAIC data. The considered set of stations covers a range of altitudes between 115 and 3580 m and therefore allows to improve our knowledge on the vertical distribution of ozone in the lower troposphere.

Decadal trends in mean tropospheric ozone level were first discussed. The most recent series of measurements (2001–2004) at the French station Pic-du-Midi (2877 m) does not show any trend since the early 1990s, and therefore does not continue the

rapid increase during the 1980s. Other data or studies (surface data at Alpine sites, MOZAIC airborne data) confirm a trend that has slowed down but remains positive (0.5–0.9 ppb/yr).

The main focus of the study was on the vertical distribution of ozone mixing-ratio and variability in the lower troposphere. The mean ozone levels (multi-annual average) at the surface stations appear to follow closely the mean vertical profile given by MOZAIC, characterized by a sharp positive gradient (30 ppb/km) in the first kilometre, a transition layer around 1000 m, and a slower increase above (about 3 ppb/km). This first points out that ozone mixing-ratio is a highly stratified field in the lower troposphere. Therefore the station altitude and even, the possible role of rapid vertical transport, should be considered as key elements for the interpretation of ozone surface data. The agreement between surface and free-troposphere data at similar elevation was not a priori evident (due to possible surface effect on ozone level). To some extent this result qualifies mountain stations to monitor long-term changes in ozone.

Investigation of ozone variability as a function of altitude confirms that levels around 1000 m mark a rather clear transition between boundary-layer and free-tropospheric regimes for ozone, especially in summer when photochemistry account for about the third of the variability in the lowest kilometre whereas only less than 20% above where day-to-day changing weather conditions (and perhaps also transport of ozone at the synoptic scale) cause most of ozone variability.

Nevertheless day-to-day net photochemical production in the boundary layer remains detectable at high-altitude sites during sufficiently lasting pollution episodes at the regional scale – in general in summer. Such episodes influence ozone monthly means at all altitudes. Maxima may appear for summer months (June to September) in addition to the spring tropospheric maximum (April–May). As a result the ozone level remains more or less constant and high in spring and summer – what is known as the broad summer maximum. An complementary and newer result concerns variability, that is clearly higher (even in relative value) during summer than spring. This confirms that spring and summer maxima have causes of different natures and at different scales.

Downscaling in time, one above mentioned result was the strong dependence of ozone sub-daily variability on station altitude. This opens the question of the diurnal variation of ozone observed at various altitudes, that will be addressed in detail in a coming paper.

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| Site | Abbrev. | Altitude (m) | Ozone (ppb) 2001–2004 | Description | Organisation |
|---|---|---|---|---|---|
| Brotonne | BRO | 115 | 25.3±6.3 | plain, forest | MERA |
| La Tardière | TAR | 143 | 30.4±7.4 | plain, forest | MERA |
| Peyrusse | PEY | 200 | 32.8±7.3 | plain, forest, grassland | MERA |
| Revin | REV | 390 | 30.3±8.8 | plain, forest | MERA |
| Morvan | MOR | 620 | 31.8±7.4 | plain, forest | MERA |
| Noia | NOI | 685 | 40.3±6.3 | | WDCGG |
| Montandon | MON | 746 | 28.4 ± 8.3 | plain, forest | MERA |
| Donon | DON | 755 | 38.9±9.7 | Vosges Mountains, forest | PAES |
| Castaneda | CAST | 770 | 39.5±12.2 | Pre-Alps, hillside | GR |
| Zimmerwald | ZIM | 898 | 36.6±9.8 | hill | BE |
| San Pablo de los Montes | SAN | 917 | 45.2±8.7 | | WDCGG |
| Hohenpeissenberg | HOH | 985 | 41.5±10.3 | top of a hill | WDCGG |
| Zugerberg | ZUG | 990 | 38.3±13.7 | Top of a hill, pasture | IAP |
| Rigi-Seebodenalp | RIG | 1031 | 42.3±10.3 | Pre-Alps, on a terrace, pasture | NABEL |
| Chaumont | CHA | 1137 | 43.3±9.9 | Jura, on a ridge, pasture | NABEL |
| Schauinsland | SCH | 1205 | 43.4±9.1 | | WDCGG |
| Iraty | IRA | 1400 | 46.4±5.8 | high station, top of forest, dry plateau | MERA |
| Puy de Dôme | PDD | 1465 | 44.9±9.8 | high station, on the top, pasture | PAES |
| Davos | DAV | 1638 | 42.0±7.1 | Pre-Alps, slope, forest | NABEL |
| Le Casset | CAS | 1750 | 46.8±7.4 | high station, slope | MERA |
| Arosa | ARO | 1840 | 42.3±8.2 | Pre-Alps, high mountains around | GR |
| Wengernalp | WEN | 1890 | 46.8±7.1 | slope, top of the hill, pasture and forest | IAP |
| Monte Cimone | MDC | 2165 | 52.8±9.0 | | WDCGG |
| Pic du Midi | PDM | 2877 | 48.3±6.8 | high station, on the top | PAES |
| Zugspitze | ZSP | 2960 | 51.5±13.7 | high alpine, top | WDCGG/IMK-IFU** |
| Sonnblick | SON | 3106 | 51.4±6.5 | high alpine | WDCGG/Umw.* |
| Jungfraujoch | JUN | 3580 | 53.3±6.8 | high alpine, on a saddle, ice | NABEL |

**Table 1.** Characteristics of the measurement sites used in this study. * Umw.: Umweltbundesamt Österreich (Federal Environmental Agency of Austria). ** IMK-IFU: Institut für Meteorologie une Klimaforschung (Germany, Forschungszentrum Karlsruhe)

| Station | Source | Period | Ozone (ppb) | Trend |
|---|---|---|---|---|
| JUNGFRAUJOCH | Schuepbach et al. (2001) | 1988–1997 | 49.3 | + 0.8 %.yr$^{-1}$(+ 0.4 ppb.yr$^{-1}$) |
| | Brönniman et al. (2000) | 1992–1998 | 50.2 | + 0.9 %.yr$^{-1}$(+ 0.5 ppb.yr$^{-1}$) |
| | this analysis | 2001–2004 | 53.3 | |
| SONNBLICK | Scheel et al. (1997) | 1989–1993 | 47.5 | + 0.7 %.yr$^{-1}$(+ 0.4 ppb.yr$^{-1}$) |
| | this analysis | 2001–2004 | 51.4 | |
| ZUGSPITZE | Scheel et al. (1997) | 1989–1993 | 48.5 | + 0.6 %.yr$^{-1}$(+ 0.3 ppb.yr$^{-1}$) |
| | this analysis | 2001–2004 | 51.5 | |
| PIC DU MIDI | Marenco et al. (1994) | 1990–1993 | 47–49 | = |
| | this analysis | 2001–2004 | 48.3 | |
| MT. CIMONE | Bonasoni et al. (2000) | 1996–1998 | 53 | = |
| | this analysis | 2001–2004 | 52.8 | |
| MOZAIC Frankfurt | Zbinden et al. (2006) | 1994–2002 | | + 0.7 ppb.yr$^{-1}$ |
| MOZAIC Paris | Zbinden et al. (2006) | 1994–2002 | | + 0.9 ppb.yr$^{-1}$ |

**Table 2.** Ozone averaged levels for high stations (above 2000 m) for different periods starting around the early 1990s. Trends are calculated from ozone averaged levels in the 1990s provided by the literature and those betwwen 2001 and 2004.



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7, 1327–1356, 2007

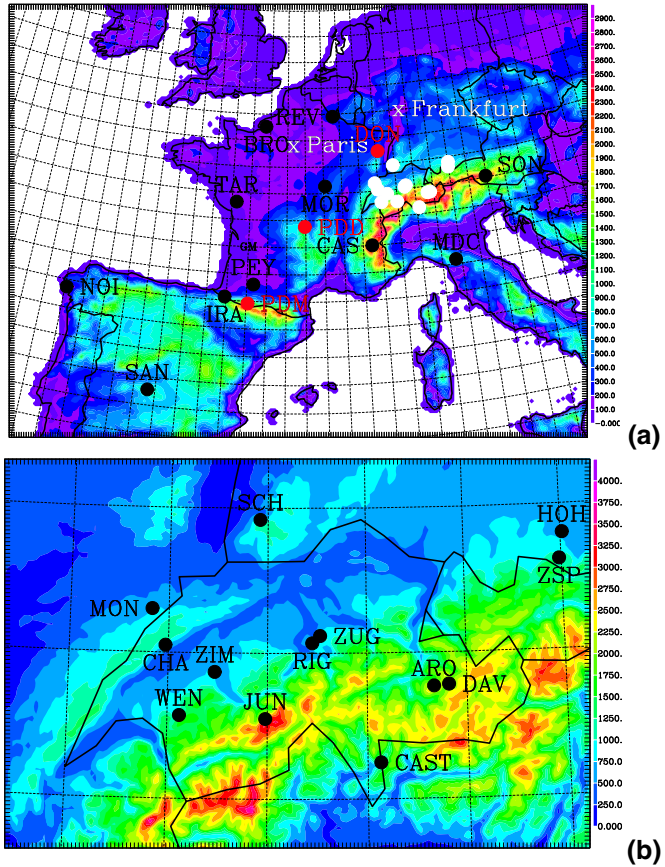


**Fig. 1.** **(a)** Location of the monitoring sites used in this study; **(b)** zoom on Swiss sites. See correspondence between station full names and abbreviations in Table 1.



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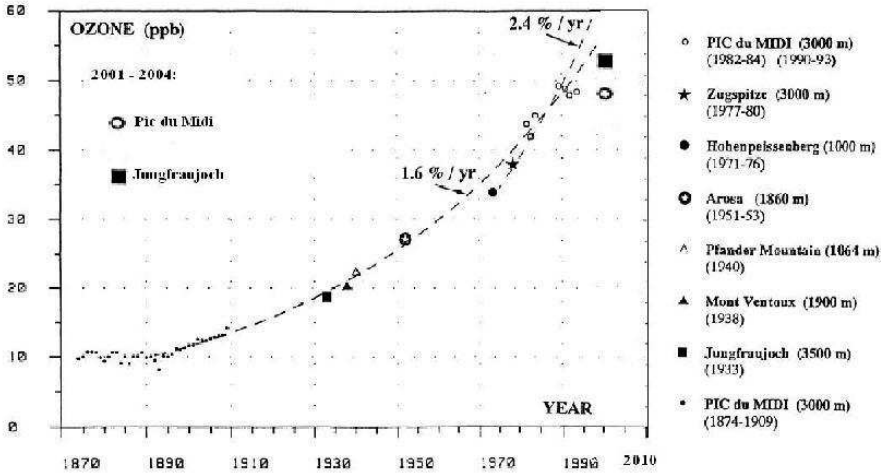


**Fig. 2.** Ozone evolution in the free troposphere over western Europe, extracted from Marenco et al. (1994) completed with mean mixing-ratio at JUN and PDM between 2001 and 2004.



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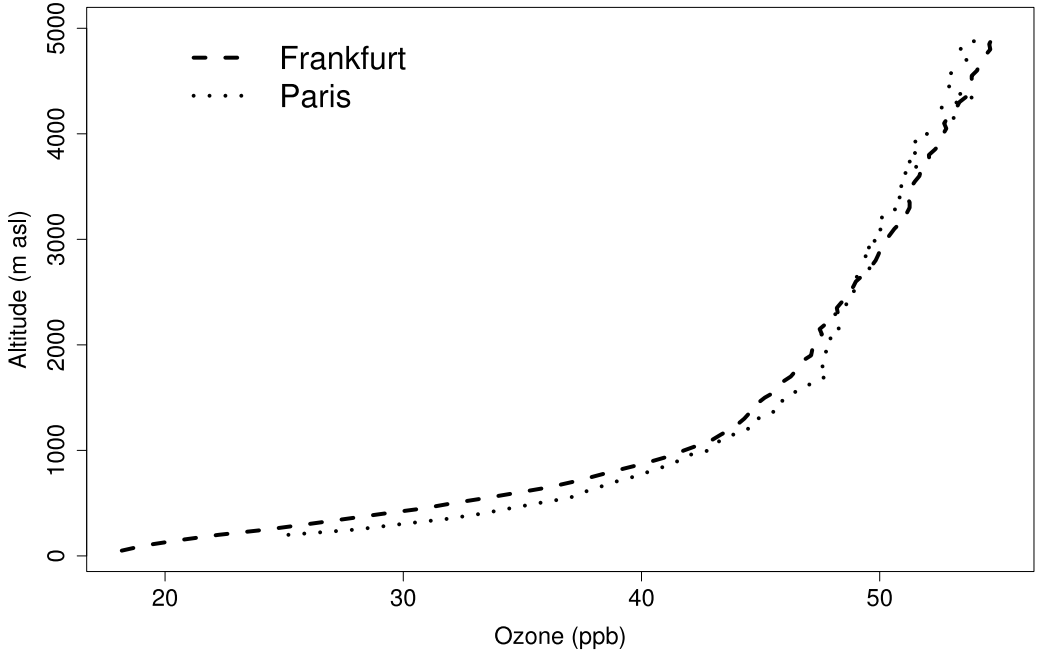


**Fig. 3.** Comparison between MOZAIC mean ozone profiles above Paris and Frankfurt over the period January 2001–July 2004.

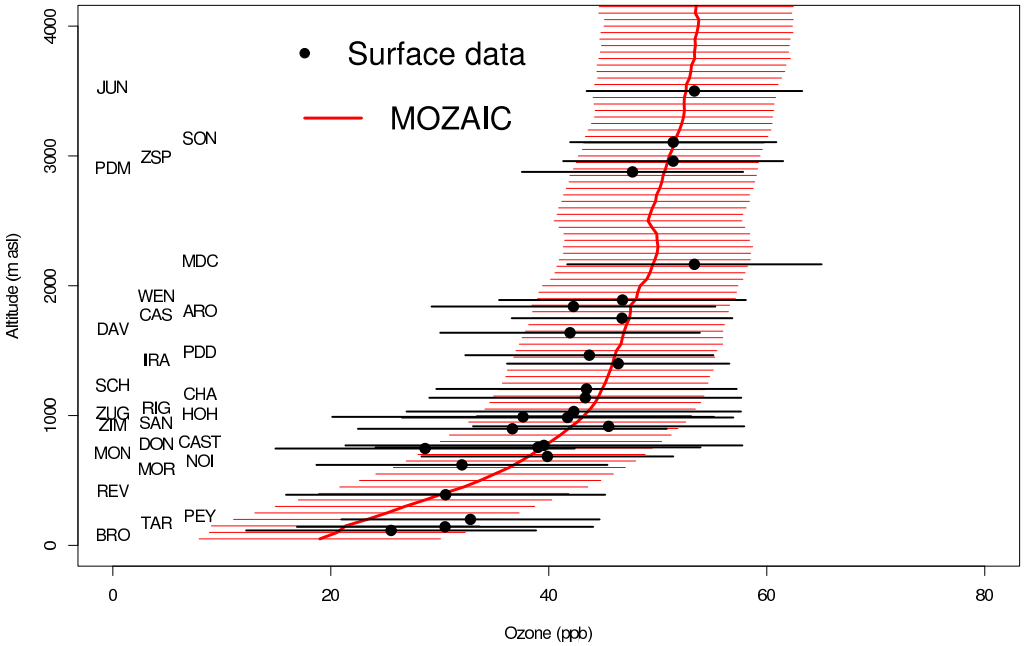


**Fig. 4.** Comparison between MOZAIC profiles above Frankfurt (bold red line: monthly mean ozone level; light red bars: ±1 standard deviation) and data from surface stations (black dots: monthly mean ozone level; black bars: ±1 standard deviation) during the period January 2001–July 2004 (when MOZAIC data are available). The statistics (standard deviation) are based on hourly data (statistics based on daily data gave similar results).



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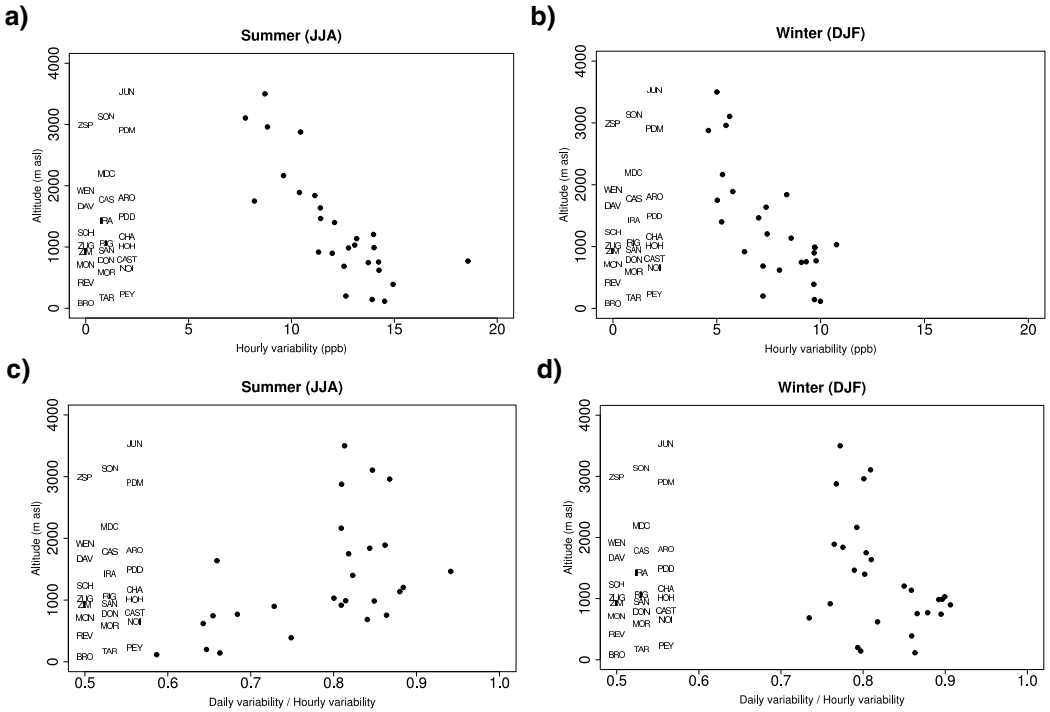


**Fig. 5.** Variability (standard deviation) of hourly surface ozone data during the period 2001-2004 for **(a)** summer and **(b)** winter. Ratio of daily variability to hourly variability for **(c)** summer and **(d)** winter.



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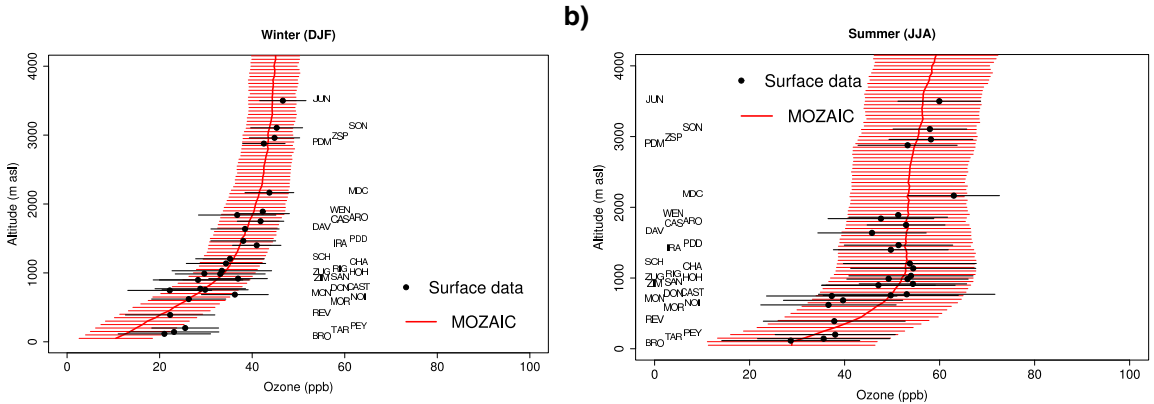


**Fig. 6.** As Fig. 4 for **(a)** winter (DJF) and **(b)** summer (JJA).



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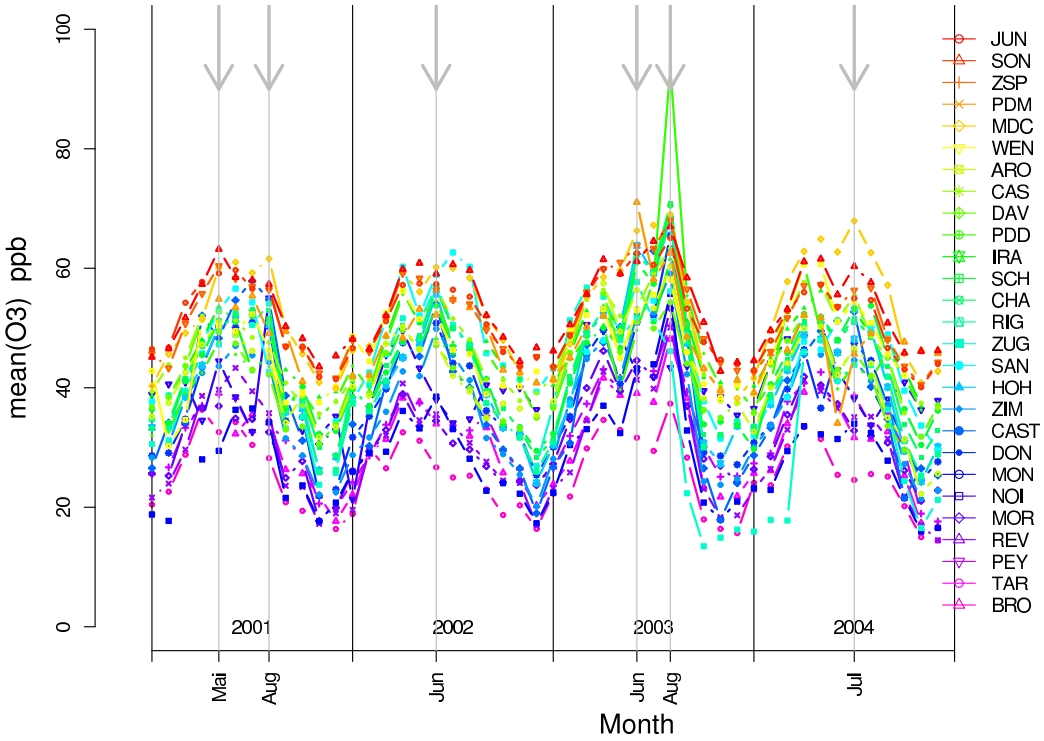


**Fig. 7.** Monthly averaged ozone mixing ratios (ppb) for all stations (sorted and colored by growing altitude). Arrows: see explanation in Fig. 8.



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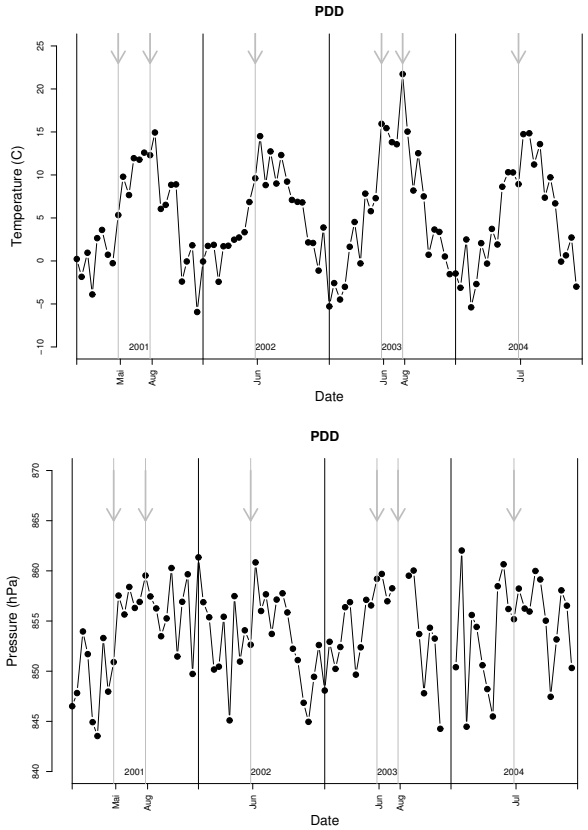


**Fig. 8.** 15 day-averaged temperature **(a)** and pressure **(b)** at PDD between 2001 and 2004. Arrows indicate the occurrence of lasting anticyclonic episodes and accompanying heat-waves.



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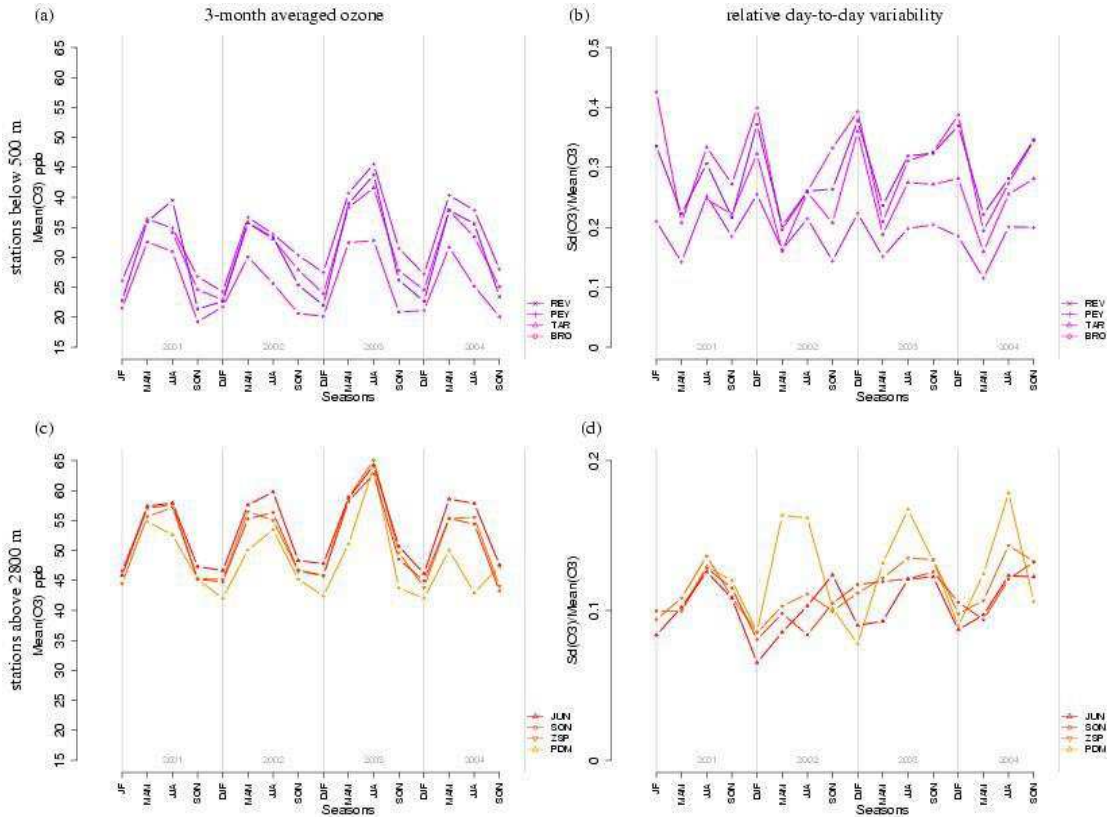


**Fig. 9. (a)** Seasonal (3-month) averaged ozone mixing ratio and **(b)** relative day-to-day variability (i.e., standard deviation based on the daily data divided by seasonal mixing ratio) for stations below 500 m. **(c-d)** as (a,b) but for stations above 2800 m.



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